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(54) Cathode ray tube with single crystal targets.

(57) Light output of single crystal phosphors used on cathode ray tubes can be vastly improved by use of a microfaceted surface structure conveniently produced by use of a single crystal epitaxial layer (e.g. 32) with lattice constant slightly larger than the single crystal substrate (e.g. 31). Such epitaxial layers are conveniently grown using substituents that increase the lattice constant compared to the single crystal substrate.

FIG. 3
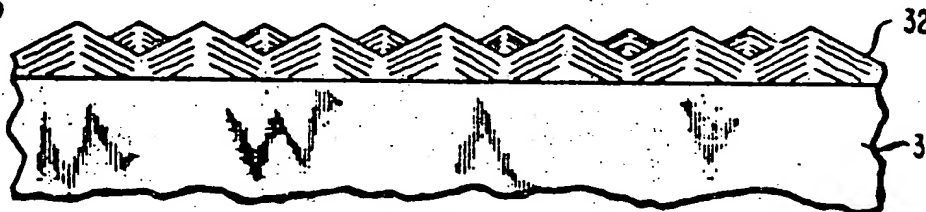
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CATHODE RAY TUBE WITH SINGLE CRYSTAL TARGETS

Technical Field

The invention involves a cathode ray tube with single crystal targets and a method of making such cathode ray tubes.

Background of the Invention

Cathode ray tubes are used extensively in a variety of display applications including direct view and projection television sets, monitors for computer terminals, television and avionics systems, etc. In many applications (such as projection tubes), high image brightness is required which can only be obtained by the use of a very high power density electron beam. Such high power densities often degrade conventional cathode ray tubes and therefore limit the lifetime of high intensity cathode ray tubes.

A significant advance in the development of high intensity cathode ray tubes was the discovery that certain luminescent epitaxial garnet films on single crystal substrates could withstand much higher power densities than with polycrystalline phosphors without tube degradation (see, for example, J. M. Robertson et al., Applied Physics Letters , 37 (5), pp. 471-472, September 1, 1980). Several systems were examined using yttrium aluminum garnet as the substrate and various activators in yttrium aluminum garnet in the epitaxial layers. The activators examined were Tb, Eu, Pr, Tm and Ce. The epitaxial layers were grown by liquid phase epitaxy using a $PbO-B_2O_3$ flux.

These types of fluorescent screens did indeed withstand much higher electron power densities than conventional screens and maintained their performance without long term degradation. Because of the magnitude of the index of refraction (1.84 at 550 nm for yttrium aluminium garnet), a large fraction of the light generated within the single crystal luminescent screen is trapped by internal reflection. It is highly desirable to increase the fraction of generated light extracted from the single crystal screen.

Various proposals have been made to increase the amount of light exiting the single crystal cathode ray tube. One proposal, described by P. F. Bongers et al. in U. S. Patent 4,298,820 issued on November 3, 1981, has a surface epitaxial layer on the luminescent screen with V-shaped grooves. These grooves increased the amount of light exiting the tube. The pattern of grooves was produced by an etching procedure on the epitaxial film, but such a procedure is difficult to carry out on such chemically stable crystals as yttrium aluminum garnet. An alternative procedure, described by I. F. Chang et al., IBM Technical Disclosure Bulletin, 25 (5), 1982, page 2630, involves the immersion of the garnet layer in a fluxed melt at a temperature above the saturation temperature of the fluxed melt. This procedure leads to dissolution of part of the epitaxial layer to form a facet surface structure. An alternative approach is to form facets on the single crystal substrate via etching prior to the growth of the luminescent layer.

Single crystal cathode ray tubes would be much more attractive commercially if a simple, easily made structure could be devised to couple light out of the structure. Particularly attractive would be a process which was easy, reliable, and attractive from a commercial fabrication point of view. In particular, the surface structure of the tube and process for making the tube should not induce detrimental mechanical defects in the cathode ray tube, adversely affect the cathodoluminescence efficiency, and preferably be applicable to a wide variety of crystal orientations and material systems.

Summary of the Invention

The invention is a cathode ray tube in which the tube face comprises single crystal substrate at least partially covered by epitaxial film with microfaceted surface. These pyramid-like structures have a base dimension of typically approximately 3-10 μm and serve as a very effective method of enhancing luminous output of a single crystal faceplate of a cathode ray tube. Generally, the epitaxial layer is of such composition (usually close but not exactly the same as the composition of the single crystal substrate) that the lattice parameter is slightly larger for the epitaxial layer than the single crystal substrate. Also included in the invention is a method of making such a microfaceted CRT faceplate. Here, an epitaxial layer, with composition so that the lattice constant is slightly larger than that of the substrate, is grown on the substrate. The epitaxial layer is grown by liquid phase epitaxial process discussed in a number of

references including "The Growth of Magnetic Garnets by Liquid Phase Epitaxy," by S. L. Blank and J. W. Nielsen, Journal of Crystal Growth, 17 (1972), pp. 302-311, and "Bubble Domain Memory Materials," by James W. Nielsen, IEEE Transactions on Magnetics, Vol. MAG-12, No. 4, July 1976, pp. 327-345. Growth of such a composition produces facets which greatly enhance the amount of light exiting the faceplate.

5   The microfaceted surface is part of an epitaxial layer on the single crystal faceplate with composition such that the lattice constant at ambient temperatures is at least 0.0005 to 0.004 nm larger than the substrate. Where the lattice constant of the epitaxial layer is less than about 0.0005 nm larger than the substrate, faceting usually does not occur; greater than about 0.0075 nm, epitaxial growth usually does not occur. Preferred limits are 0.0015 to 0.0065 nm and most preferred limits are 0.0045 ± 0.0015 nm. Such
10   cathode ray tubes exhibit enhanced light output compared to conventional cathode ray tubes operated under the same cathode luminescence conditions. Also, luminescence efficiency is not degraded by the composition changes necessary to produce the microfaceted faceplate. Furthermore, the fabrication procedure is relatively easy to carry out and is adaptable to mass production.

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Brief Description of the Drawing

     FIG. I shows a schematic cross-sectional view of a cathode ray display device; ·
     FIG. 2 shows in graphical form data on lattice constant in the yttrium aluminum garnet-yttrium gallium
20   garnet crystal system; and
     FIG. 3 is an edge view of a single crystal faceplate with microfaceted structure made in accordance with the invention.

25   ## Detailed Description

     The invention is based on the discovery that epitaxial layers grown on single crystal substrates, where the lattice constant of the epitaxial layer is slightly larger than the lattice constant of the substrate, yields a microfaceted structure useful in a variety of applications. The microfaceted configuration is particularly
30   useful for coupling light out of a transparent structure (e.g., disc or rectangular plate, etc.) with a high index of refraction where much of the light is trapped inside the transparent structure due to total internal reflection. Attractive applications are to single crystal faceplates on cathode ray tubes where the faceplate on the tubes is single crystal with high index of refraction. The microfaceted structure is composed of small pyramid-like structures having a typical base dimension of approximately 3-I0 μm. They serve as an
35   effective method of enhancing luminous output of a cathode ray tube and are particularly useful for projection cathode ray tubes with single crystal faceplates for the cathode ray tube.
     The invention is typically applicable to cathode ray tubes with single crystal faceplates such as yttrium aluminum garnet, yttrium scandium aluminum garnet ($Y_3ScAl_4O_{12}$), and gadolinium gallium garnet. Generally, the single crystal used as the faceplate should be largely transparent, capable of being grown in the form of
40   large single crystals for fabrication into substrates capable of activation for cathodoluminescence either by doping directly or doped epitaxial layers on the single crystal, and be otherwise suitable for use of cathode ray tubes. A large variety of single crystal materials may be used in the practice of the invention includ' ig, for example, barium hexa-aluminate, yttrium orthosilicate, and the garnet system. The garnet system, particularly those mentioned above, are preferred because of their excellent cathodoluminescence prop-
45   erties, ease of growth of bulk crystals and ease of growing epitaxial layers upon the garnet substrate.
     Various structures of the faceplate may be used consistent with the practice of the invention. Generally, the microfaceted structure is located in an epitaxial layer, adjusted in composition so that the microfaceted structure forms on growth. Typically, this is done by fixing the composition of the epitaxial layer so that the lattice constant is slightly larger than the lattice constant of the substrate. The activator ions (typically
50   phosphorescent ions such as Ce^{+3}, Tb^{+3}, etc.) may be present in this epitaxial layer, in another epitaxial layer on top of the epitaxial layer containing the microfacets, or in the substrate. Generally, the first two alternatives are preferred since in the latter case where the activator ions are located in the substrate, the electron beam must penetrate the epitaxial layer before entering the activated region.

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The faceplate structure described above is most usefully used in a cathode ray tube, generally one designed for high image brightness, either for use in a projection system or in the presence of high-background light. A typical cathode ray tube is shown in FIG. I. The cathode ray tube $\underline{10}$ is made up of an electron radiation source, II, with means for electrical connection to outside source of electrical signal, an enclosure usually made of glass I3, a single crystal substrate I4 with microfaceted structure and activated region I5.

Particularly useful in an understanding of the invention is a description of several specific particular systems. Yttrium aluminum garnet is a readily available faceplate material which has excellent qualities such as good cathodoluminescent properties when properly doped, ability to withstand high electron-beam densities without saturation or damage, and well-developed procedure for growing epitaxial layers. Also, gallium can be substituted for aluminum for the gradual increase in the lattice constant for use in the epitaxial layer with microfaceted structure.

The composition of the epitaxial layer depends on the substrate and amount of increased lattice constant required to produce the microfaceted structure. FIG. 2 shows, for the yttrium aluminum garnet-yttrium gallium garnet system, a graph of lattice constant versus garnet composition. The lattice constant of pure yttrium aluminum garnet is I.2007 nm; of pure yttrium gallium garnet I.2280 nm. Each mole of gallium substituted for aluminum increases the lattice constant of yttrium aluminum garnet by +0.00546 nm. Typically, smaller amounts of expansion are most useful, generally of the order of 0.0015-0.0075 nm.

The Tb^{+3} activated yttrium aluminum garnet system provides an excellent illustration of the invention. Conventionally, a Tb^{+3} activated yttrium aluminum garnet film is grown on a yttrium aluminum garnet single crystal substrate to provide the cathodoluminescence needed in the cathode ray tube. This epitaxial layer conventionally has a composition of $(Y_{2.9} Tb_{0.1})Al_5O_{12}$ and is grown at high temperatures (typically around I060 degrees C) from a $PbO-B_2O_3$ flux.

The microfaceted structure is grown using a composition in which some of the aluminum is replaced by gallium to provide the increased lattice constant. The composition of the melt used to grow the epitaxial film is given in Table I. Growth was carried out at a temperature of I060 degrees C at a rate of I.67 μm/minute to yield a film with a thickness of 8.II μm. This resulted in an epitaxial film with approximate composition - $(Y_{2.9}Tb_{0.1})(Al_{4.6}Ga_{0.4})O_{12}$ which then results in a film lattice constant of approximately 0.0022 nm greater than that of $Y_3Al_5O_{12}$.

Table I

Melt Composition for Epitaxial Growth

Compound	Weight in Grams
Y_2O_3	5.917
Tb_4O_7	0.462
Al_2O_3	10.03
Ga_2O_3	6.148
PbO	1000
B_2O_3	25.61

Growth of the epitaxial layer in this way yields a microfaceted layer as shown in FIG. 3. Here is shown an edge view of a faceplate with single crystal substrate 3I and microfacted epitaxial layer 32. In the yttrium aluminum garnet-yttrium gallium garnet described above (and probably other garnet systems), the surface of the substrate is a <III> crystal plane and the facets are <II0> and <2II> planes.

Measurements were carried out to compare the light output of the tube described above with a tube without the microfaceted structure. For electron beam excitation with high power density (1×10^{10} W/m^2), the microfaceted tube prepared from the melt of Table I has about 23 percent more light output under identical conditions than the tube without a microfaceted epitaxial layer. For low power density excitation (10^6 W/m^2), the improvement in light output is about 50 percent.

As mentioned above, the microfaceted structure may be made without the phosphor activator ions in the microfaceted layer and with the phosphor epitaxial layer over the microfaceted epitaxial layer. The microfaceted epitaxial layer is grown on a substrate of yttrium aluminum garnet using a melt composition which yields the approximate composition $Y_3(Al_{4.6}Ga_{0.4})O_{12}$ in the microfaceted layer. Melt composition for growth of this microfaceted layer is given in Table II.

Table II
Melt Composition For Growing Epitaxial Microfaceted Layer on Yttrium Aluminum Garnet

Compound	Weight in Grams
Y_2O_3	10.00
Al_2O_3	16.95
Ga_2O_3	13.35
PbO	1500
B_2O_3	38.87

The microfaceted epitaxial layer was grown at 1080 degrees C at a growth rate of 1.53 μm/minute to a thickness of 10.10 μm.

The epitaxial phosphor layer is then grown on top of this microfaceted layer using a melt composition set forth in Table III to yield an epitaxial layer composition of $(Y_{2.785} Ce_{0.015} Tb_{0.2})(Al_5O_{12})$. The phosphor epitaxial layer is grown at 1008 degrees C at a rate of 4.05 μm/minute to a thickness of 5.67 μm.

Table III
Melt Composition For Growing Epitaxial Activated Layer on Microfaceted Layer

Compound	Weight in Grams
Y_2O_3	10.00
CeO_2	4.052
Tb_4O_7	1.76
Al_2O_3	16.95
PbO	1640
B_2O_3	42.49

The similar degree of microfacet formation which results from the two layer structure of (a) facet producing layer from a melt of composition given in Table II, and (b) a luminescent layer from the melt of composition given in Table III produce similar performance enhancement. For high power density excitation (1 × 10^{10} W/m^2), the improvement is 35 percent relative to a tube fabricated without microfaceted epitaxial layers. At conditions of low power excitation (1 × 10^6 W/m^2), the performance improvement was 32 percent.

Another example for preparation of the microfaceted epitaxial film by partial substitution of aluminum by gallium is given by growth of epitaxial film from the melt composition given in Table IV.

Table IV Melt Composition for Epitaxial Growth	
Component	Weight in Grams
Y_2O_3	7.700
Tb_4O_7	0.600
Lu_2O_3	0.0
Al_2O_3	13.030
Ga_2O_3	21.970
PbO	1250
B_2O_3	33.40

Film growth was carried out at a temperature of approximately 1058 degrees C and a growth rate of 1.72 μm/minute to yield a film thickness of approximately 5.16 μm. This resulted in an epitaxial film with the approximate composition $(Y_{2.9}Tb_{0.1})(Al_4Ga_1)O_{12}$, which has a lattice constant of approximately 0.0056 nm greater than the $Y_3Al_5O_{12}$ substrate.

With the growth of a $(Y_{2.9}Tb_{0.1})(Al_4Ga_1)O_{12}$ epitaxial film, the amount of lattice constant mismatch is much in excess of that considered feasible from previous literature on epitaxial growth of rare earth garnets from the PbO/B$_2$O$_3$ flux. (See Blank and Nielsen and Nielsen cited previously.)

To assess the performance of the microfacted film grown from the melt of Table IV, sufficient Lu$_2$O$_3$ was added to modify the composition to that listed in Table V. Growth of an epitaxial film was performed at 1049 degrees C and a growth rate of 2.35 μm/minute for a period of time to produce a 4.70 μm thick film.

Table V	
Melt Composition For Epitaxial Growth	
Component	Weight in Grams
Y_2O_3	7.70
Tb_4O_7	0.60
Lu_2O_3	13.50
Al_2O_3	13.03
Ga_2O_3	21.97
PbO	1750
B_2O_3	46.40

The performance of the microfacted epitaxial phosphors grown from melts in Tables IV and V are summarized in Table VI for both high and low power electron beam excitation. The performance data is given normalized to a reference specimen of known luminescent efficiency. This is done to demonstrate that the luminescence from the epitaxial film without microfacets ($\approx$ 0.7) is as expected from other studies on Tb^{3+} activated garnet phosphors with partial Ga^{3+} substitution for Al^{3+} (G. W. Berkstresser, J. Shmulovich, D. T. C. Huo, G. Matulis, C. D. Brandle and A. J. Valentino, October 14-18, 1985, the Electrochemical Society meeting).

Given the expected performance of the luminescent phosphor composition without microfacets, the preparation of a tube with the microfacet epitaxial layer from the melt of composition given in Table IV yields an improvement of 330 percent at high power and 280 percent for low power density excitation.

Table VI		
Faceted Faceplate Performance		
Structure	High Power	Low Power
facets	2.09	2.12
clear	0.62	0.75
reference	1.0	1.0

The garnet material $Y_3ScAl_4O_{12}$ also serves as a single crystal substrate material with the substitution of Gd for Y or Ga for Al.

Claims

1. A device, such as a cathode ray tube, comprising a faceplate, said faceplate comprising single crystal substrate and epitaxial layer contacting at least part of the surface of the single crystal substrate, CHARACTERIZED IN THAT
the lattice constant of the epitaxial layer is between 0.0005 and 0.0075 nm, preferably 0.0015 to 0.006 nm larger than the lattice constant of the single crystal substrate and the epitaxial layer has a microfaceted surface structure.

2. The device according to claim I,
CHARACTERIZED IN THAT
the base dimensions of the microfacets are about 3-10 μm.

3. The device according to claim I,
CHARACTERIZED IN THAT
the lattice constant of the epitaxial layer is 0.0045 ± 0.0015 nm larger than the lattice constant of the single crystal substrate.

4. The device according to claim I,
CHARACTERIZED IN THAT
the single crystal substrate comprises transparent garnet crystal.

5. The device according to claim 4,
CHARACTERIZED IN THAT
the garnet crystal is selected from yttrium aluminum garnet, yttrium scandium aluminum garnet and gadolinium gallium garnet.

6. The device according to claim I,
CHARACTERIZED IN THAT
the epitaxial layer or the single crystal substrate or both comprises activator ion.

7. The device according to claim I,
CHARACTERIZED IN THAT
the epitaxial layer is at least partially covered with a second epitaxial layer, said second epitaxial layer comprising activator ion.

8. A process for making a device according to any one of preceeding claims I-8, which comprises the step of immersing the single crystal substrate into a molten composition at a temperature so as to grow an epitaxial layer with composition such that the lattice constant is 0.0005 to 0.0075 nm larger than the lattice constant of the single crystal substrate.

9. The process according to claim 8,
CHARACTERIZED IN THAT
the single crystal substrate is yttrium aluminum garnet and the epitaxial layer has approximate composition of $(Y_{2.9}Tb_{0.1})(Al_{4.0}Ga_{1.0})O_{12}$ or $Y_3(Al_{4.6}Ga_{0.4})O_{12}$.

I0. The process according to claim 9,
CHARACTERIZED IN THAT
the melt composition for epitaxial growth of $(Y_{2.9}Tb_{0.1})(Al_{4.0}Ga_{1.0})O_{12}$ is that resulting from mixing together 7.70 grams of Y_2O_3, 0.60 grams of Tb_4O_7, I3.03 grams of Al_2O_3, 2I.97 grams of Ga_2O_3, I250.0 grams of PbO and 32.36 grams of B_2O_3, and carrying out the growth at a temperature of approximately I063 degrees C.

II. The process according to claim 9,
CHARACTERIZED IN THAT
the melt composition for epitaxial growth of $Y_3(Al_{4.6}Ga_{0.4})O_{12}$ is that resulting from mixing I0.00 grams of Y_2O_3, I6.95 grams of Al_2O_3, I3.35 grams of Ga_2O_3, I500 grams of PbO and 38.87 grams of B_2O_3, and carrying out the growth at a temperature of approximately I080 degrees C.

I2. The process according to claim I,
CHARACTERIZED BY
growing on the microfaceted layer an additional epitaxial layer with approximate composition $(Y_{2.785}Ce_{0.015}Tb_{0.2})(Al_5O_{12})$

I3. The process according to claim I2,
CHARACTERIZED IN THAT
the additional epitaxial layer is grown at an approximate temperature of I008 degrees C from a melt composition that results from mixing I0.0 grams of Y_2O_3, 4.052 grams of CeO_2, I.76 grams of Tb_4O_7, I6.95 grams of Al_2O_3, I640 grams of PbO and 42.49 grams of B_2O_3.
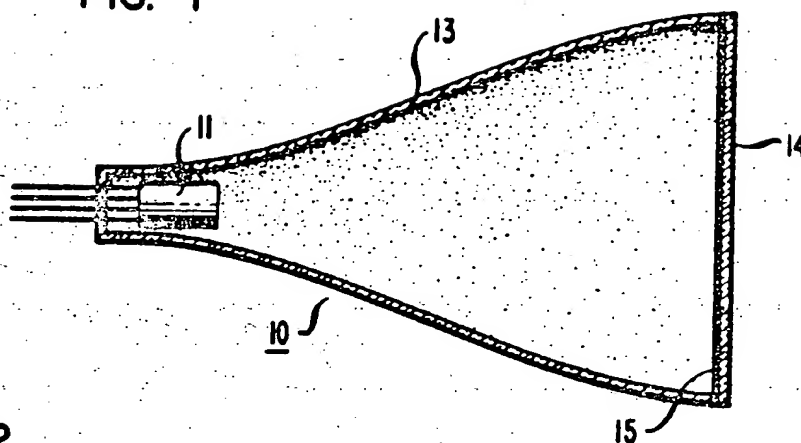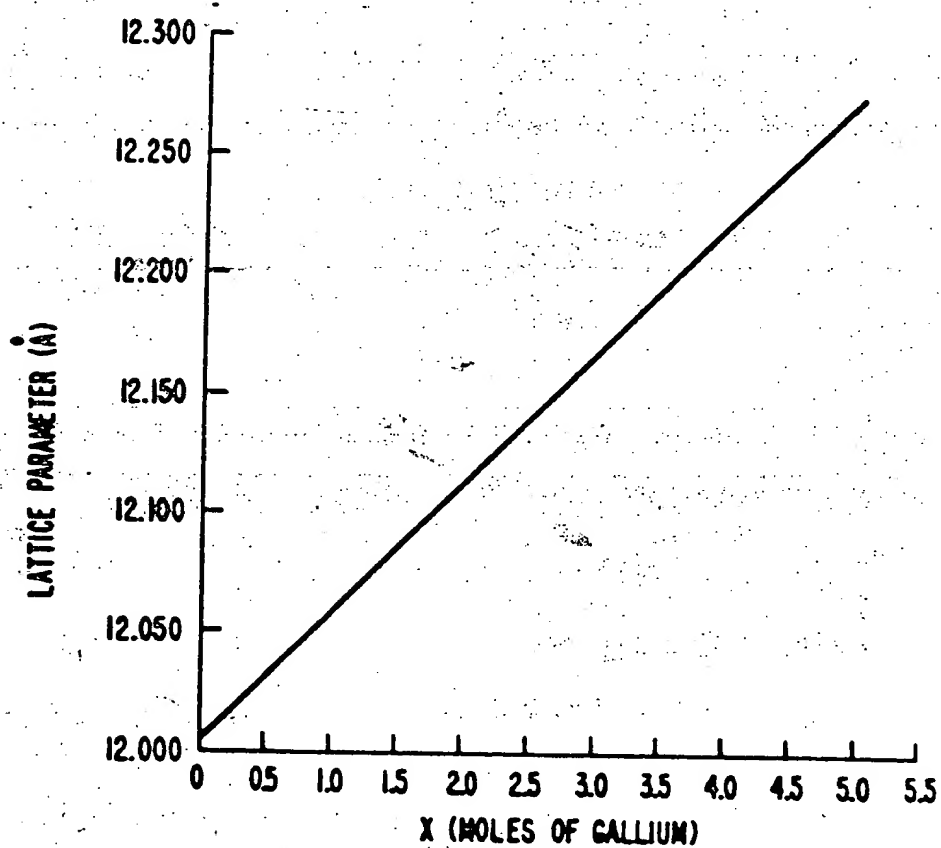
FIG. 1

FIG. 2

FIG. 3